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# NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF PHOSPHORUS

GCA Corporation

PREPARED FOR
Environmental Protection Agency

May 1973

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A national inventory of the sources and emissions of the element phosphorus was conducted. All major sources of phosphorus-containing emissions were identified and their phosphorus emissions into the atmosphere estimated. Also, a method for updating the results of the study every two years was recommended.

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by

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Contract No. 68-02-0601

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Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

May 1973

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## ABSTRACT

A national inventory of the sources and emissions of the element phosphorus was conducted. The study included the preparation of an overall material flow chart depicting the quantities of phosphorus moving from sources of mining and importation through all processing and re-processing steps to ultimate use and final disposition. All major sources of phosphorus-containing emissions were identified and their phosphorus emissions into the atmosphere estimated. A regional breakdown of these sources and their emissions was also provided. The physical and chemical nature of the phosphorus-containing emissions was delineated to the extent that information was available, and a methodology for updating the results of this study every two years, was recommended.


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# I. INTRODUCTION

## A. PURPOSE AND SCOPE

The Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) has contracted with GCA Technology Division to conduct a national inventory of the sources and emissions of the element phosphorus. The purpose of the study was to define as accurately as possible, based on existing and available published and unpublished information, the levels, nature and sources of phosphorus-containing emissions for defined geographic regions throughout the United States.

The scope of this program is outlined below:

- Develop an overall material flow chart depicting the quantities of phosphorus moving from sources of mining and importation, through all processing and reprocessing steps to ultimate use and final disposition as far as the movements can be traced.

- Identify all major potential phosphorus-containing emission sources and estimate the total quantity of phosphorus emitted to the atmosphere from each source. Emission factors and level and types of air pollution control will also be provided for each of these sources to the extent that available information permits.

- Define those sources which contribute at least 80% of the total emissions of phosphorus.

- Provide a regional breakdown of these major sources and their emissions.

- Present the nature of the phosphorus-containing emissions for each of these major sources including a delineation of their physical and chemical form and particle size distribution to the extent that information is available.

- Provide recommendations as to a methodology for updating the results of this study every two years.

## B. CONCLUSIONS

### 1. Material Flow

Based on available data, 11,998,000 tons of phosphate rock as $P_2O_5$ were produced in the United States. Only a small quantity was imported (41,000 tons of contained $P_2O_5$) and utilized almost exclusively in animal feed applications because of its low fluorine content.

Approximately 8,350,000 tons of $P_2O_5$ were consumed domestically with about 78 percent utilized in the manufacture of fertilizers. The other primary use was as an additive in soaps, detergents and water treatment products.

Certain assumptions made in preparing the above estimates are explained in detail in Section II.

### 2. Principal Emissions Sources

The principal source category of phosphorus-containing emissions is the fertilizer manufacturing industry which contributed an estimated 82 percent of the emissions generated in the U.S. in 1970. Triple superphosphate and ammonium phosphate plants were the largest source categories, contributing 35,700 and 30,700 tons/yr. respectively. Approximately 19 percent of $P_2O_5$ containing emissions resulted from processes outside the phosphorus industry; coal combustion and iron manufacture accounted for 13 percent and 4 percent respectively.

### 3. Regional Estimates

The region in the U.S. in which most of the phosphorus is estimated to be emitted is Region 4 (Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina and Tennessee). This region accounted for 84,400 tons of $P_2O_5$ or about 53 percent of the total emitted in the U.S. This region also had the largest emission density, estimated at 0.22 tons of $P_2O_5$ per square mile - year.

4. Nature of Emissions

Phosphorus emissions from rock processing and the fertilizer industry, which is the most significant emissions source, are primarily in the form of calcium and ammonium phosphate which are categorized as stable compounds. Little information was available on the particle size distribution of these emissions.

Emissions from elemental phosphorus manufacture are initially $P_2$ and $P_4$ fumes which oxidize quickly to form $P_2O_5$. This compound is very hygroscopic and is therefore expected to form phosphoric acid ($P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$).

5. Degree of Control

The overall level of control of phosphorus-containing emissions is estimated to have been about 87 percent in 1970. An estimated 1,203,400 tons of $P_2O_5$ were generated before control and 160,400 tons were estimated after control. The major sources of $P_2O_5$ emissions before control were phosphate rock processing (218,000 tons/yr.), fertilizer manufacturing (662,000 tons/yr.), and coal combustion (115,000 tons/yr.).

## II. OVERALL U.S. MATERIAL FLOW CHART FOR PHOSPHORUS

Figure 1* presents a flow diagram depicting the total quantities of phosphorus products moving from sources of mining and importation through the processing and reprocessing steps to ultimate use and final disposition. Each of the sources is discussed below.

In the following discussion all tonnages are expressed in terms of equivalent tons of 100 percent $P_2O_5$ unless specifically stated otherwise.

### A. U.S. PRODUCTION AND ORE PROCESSING

Three major areas in the U.S. mine and beneficiate phosphate rock: Florida and North Carolina; Tennessee; and the Western States. Total 1970 domestic production was 11,998,000 tons of phosphate rock. Production from Florida and North Carolina accounted for about 81 percent of which 98 percent was for agricultural use; Tennessee, about 8 percent; and the Western States, 11 percent.[1,2]

The actual $P_2O_5$ content in the ore varies from seven to 18 percent in Florida, to 24 to 33 percent in the Western States. This percentage usually dictates the method of beneficiation and its consumptive usage.

### B. IMPORTS AND EXPORTS OF PHOSPHATE ROCK

In 1970, 3,528,000 tons of phosphate rock, about 30 percent of the total domestic production, were exported mainly to Japan, Canada, West Germany and Italy.[1] The imported phosphate rock, around 41,000 tons, was chiefly used as animal feed because of its low fluorine content.[1]

### C. INDUSTRIAL INVENTORY

Because of a reduction of phosphate rock demand, largely due to the curtailed use of phosphorus in detergents, inventory increased by 190,000 tons.[1]

* Data in Figure 1 and in this section are left unrounded, for purposes of information control. On average, the typical statistic is accurate to within 10 percent, in the opinion of the authors.

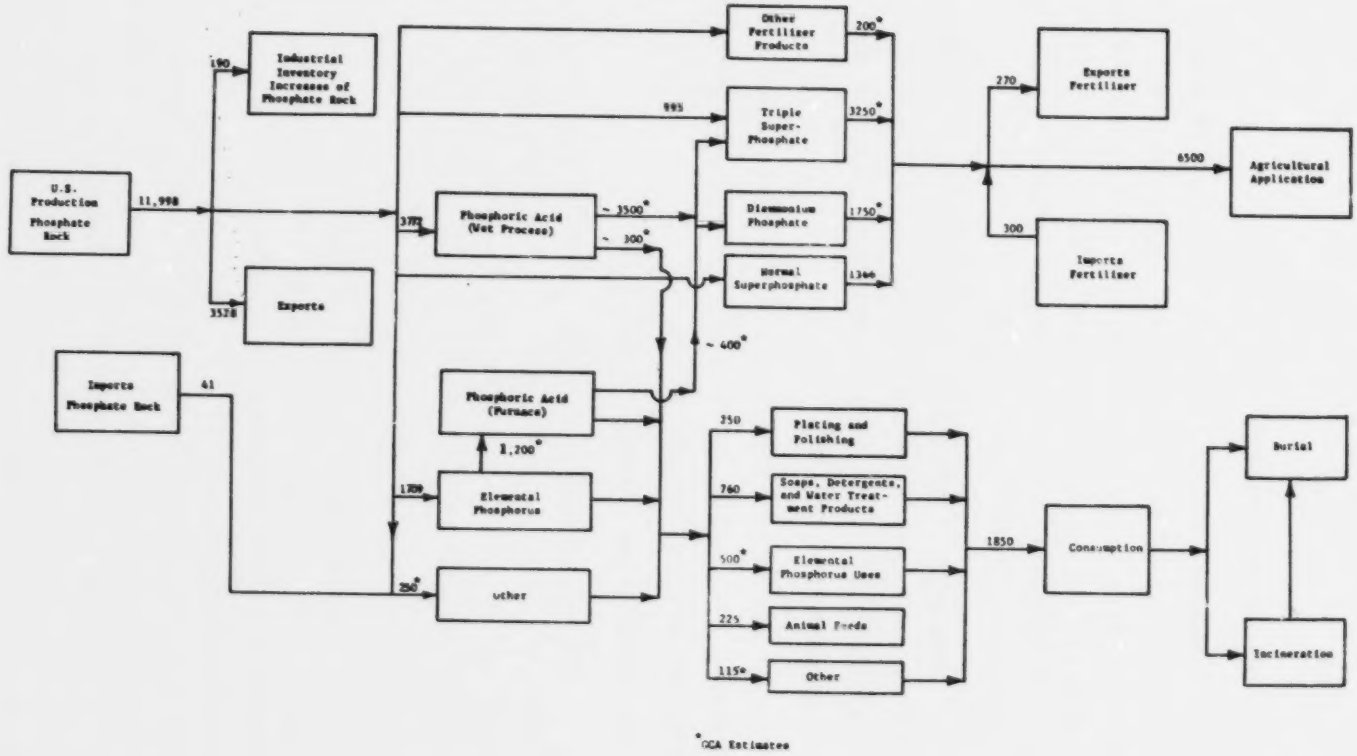


Figure 1. Phosphorus 1970 material flow
(Thousand Tons Contained $P_2O_5$)

D. FERTILIZER INDUSTRY

Phosphorus is one of the chief active components in commercial fertilizer. Many grades, both solid and liquid, are made from the numerous compounds. U.S. agriculture used about 6,500,000 tons of phosphorus primarily as normal superphosphate (1,366,000), triple superphosphate (2,250,000 tons), and diammonium phosphate, DAP, (an estimated 1,750,000 tons).[1]

More than 90 percent of the 3,772,000 tons of phosphoric acid made from the wet process goes to the fertilizer industry.[3] Therefore, about 3,500,000 tons of wet process phosphoric acid was used to make triple superphosphate and DAP.

An estimated 200,000 tons of other fertilizer products, such as pulverized phosphate rock, fertilizer filler, and other fertilizers went into agricultural application.

E. IMPORTS AND EXPORTS OF FERTILIZER

Exports of superphosphates, ammonium phosphates and mixed fertilizers amounted to 270,000 tons. Triple superphosphates from Mexico and ammonium phosphate from Canada accounted for most of the 300,000 tons imported by the U.S. for fertilizer use.[1]

F. ELEMENTAL PHOSPHORUS INDUSTRY

The production of elemental phosphorus is another major user of phosphate rock. In 1970, 1,709,000 tons were consumed,[1] of which an estimated 1,200,000 went into the production of thermal phosphoric acid and superphosphoric acid.[3-6] Most of the phosphoric acid was consumed in plating and polishing (250,000 tons),[5] and the production of sodium phosphates for soaps, detergents and water treatment (760,000 tons).[7] Approximately 500,000 tons of elemental phosphorus were used to make many compounds such as red phosphorus, phosphorus chloride, phosphorus sulfide, zinc and copper phosphide, and many other organophosphorus compounds.

## G. OTHER USES

Calcium phosphates, produced from phosphoric acid and elemental phosphorus, go primarily into animal feed supplement, with the rest used in baking power, and as a polishing agent in dentifrice. Including the imported rock, about 225,000 tons were consumed in the manufacture of animal feed.[5]

Other uses, amounting to approximately 100,000 tons, were the manufacture of calcium phosphates, ammonium phosphates, sodium phosphates, and their derivatives.[1,5]

## III. SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING EMISSIONS

### A. DATA PRESENTATION AND ACCURACY

Table 1 presents a summary of the data from which phosphorus-containing emissions in terms of $P_2O_5$ were estimated for all major potential sources. Each of the columns comprising this table will be discussed below.

#### 1. Emission Factors

Except where indicated, this gives the pounds of total particulates emitted per ton of production. Such considerations as:

- variations in process conditions among individual plants comprising a source category
- inaccuracies in existing data
- a limited quantity of existing data,

may, however, result in an average emission factor for a source category varying by more than an order of magnitude from the value presented. In recognizing the need to indicate the level of accuracy of these emission factors, a reliability code is presented along with each emission factor value appearing in the Table. This reliability code system is described below and is based on the system utilized in EPA Document No. AP-42, "Compilation of Air Pollutant Emission Factors":

A: Excellent

This value is based on field measurements of a large number of sources.

B: Above Average

This value is based on a limited number of field measurements.

C: Average

This value is based on limited data and/or published emission factors where the accuracy is not stated.

## TABLE 1

## SOURCES AND ESTIMATES OF PHOSPHORUS-CONTAINING EMISSIONS

| | Uncontrolled Particulate Emission Factor | | Reliability Code | Production Level ($10^6$ tons yr) | % $P_2O_5$ in Emissions | Reliability Code | $P_2O_5$ Before Controls ($10^3$ tons/yr) | Estimated Level of Emission Control | $P_2O_5$ Emissions After Controls ($10^3$ tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| | (lb/ton) | (Kg/$10^3$Kg) | | | | | | | |
| 1. PHOSPHATE MINING | | | | | | | | | |
| a. Land-Pebble | 0. | 0. | (D) | 115. | 10% | (B) | .0 | - | .0 |
| b. Hard-Rock | .5 | .25 | (D) | 10.2 | 26% | (B) | .7 | 0% | .7 |
| c Underground | .3 | .15 | (D) | .5 | 28% | (B) | | - | .0 |
| 2. PHOSPHATE ROCK PROCESSING | | | | | | | | | |
| Drying | 15. | 7.5 | (B) | 35. | 30% | (B) | 79. | 94% | 4.7 |
| Grinding | 20. | 10. | (C) | 35. | 30% | (B) | 105. | 97% | 3.2 |
| Calcining-Cooling | 40. | 20. | (C) | 4.0 | 30% | (B) | 24. | 95% | 1.2 |
| Material Handling | 1. | 0.5 | (C) | 39. | 30% | (B) | 5.8 | 50% | 2.9 |
| 3. PHOSPHORIC ACID (WET PROCESS) | | | | | | | | | |
| Grinding | 20. | 10. | (C) | 12. | 30% | (B) | 36. | 97% | 1.1 |
| Material Handling (ore) | 2.0 | 1. | (C) | 12. | 30% | (B) | 3.6 | 50% | 1.8 |
| Reactor, Filter, Absorber | 0.25** | .12** | (B) | 3.78 | | | - | ** | 0.5 |

**TABLE 1 (continued)**

| | Uncontrolled Particulate Emission Factor | | Reliability Code | Production Level ($10^6$ tons/yr) | % $P_2O_5$ in Emissions | Reliability Code | $P_2O_5$ Before Controls ($10^3$ tons/yr) | Estimated Level of Emission Control | $P_2O_5$ Emissions After Controls ($10^3$ tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| | (lb/ton) | (Kg/$10^3$Kg) | | | | | | | |
| 4. FERTILIZERS - (GENERAL) | | | | | | | | | |
| Rock Pulverizing | 6.0 | 3. | (C) | 7.24 | 30% | (B) | 6.6 | 80% | 1.3 |
| Material Handling | 2.0 | 1. | (C) | 7.24 | 30% | (B) | 2.2 | 0% | 2.2 |
| Screening | 2.0 | 1. | (C) | 6.5 | * | | 6.5 | 85% | 1.0 |
| Bagging | 1.0** | 0.5** | (C) | 3.2 | * | | - | ** | 1.6 |
| Bulk Loading | 1.0 | 0.5 | (C) | 3.2 | * | | 1.6 | 0% | 1.6 |
| a. NORMAL SUPERPHOS. | | | | | | | | | |
| Drying | 105. | 52.5 | (C) | 1.37 | * | | 72.0 | 90% | 7.2 |
| Cooling | 90. | 45. | (C) | 1.37 | * | | 61.7 | 90% | 6.2 |
| Product Grinding | 0.5 | 0.25 | (C) | 1.37 | * | | .3 | 80% | .1 |
| b. TRIPLE SUPERPHOS. | | | | | | | | | |
| Product Grinding | 0.5 | 0.25 | (C) | 3.25 | * | | .8 | 80% | .2 |
| Drying | 105. | 52.5 | (C) | 3.25 | * | | 171. | 90% | 17.1 |
| Cooling | 90. | 45. | (C) | 3.25 | * | | 146. | 90% | 14.6 |

TABLE 1 (continued)

| | Uncontrolled Particulate Emission Factor | | Reliability Code | Production Level ($10^6$ tons/yr) | % $P_2O_5$ in Emissions | Reliability Code | $P_2O_5$ Before Controls ($10^3$ tons/yr) | Estimated Level of Emission Control | $P_2O_5$ Emissions After Controls ($10^3$ tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| | (lb/ton) | (Kg/$10^3$Kg) | | | | | | | |
| c. AMMONIUM PHOS. | | | | | | | | | |
| Ammoniator-Granulator | 30. | 15. | (B) | 3.5 | * | | 52.5 | 85% | 7.9 |
| Drying | 55. | 27.5 | (D) | 3.5 | * | | 96.0 | 85% | 14.4 |
| Cooling | 25. | 12.5 | (C) | 3.5 | * | | 43.8 | 85% | 6.6 |
| 5. FERTILIZER APPLICATION | | | | | | | | | |
| Bagging-Bulk Loading | 1.0 | 0.5 | (C) | 6.5 | * | | 3.2 | 50% | 1.6 |
| Field Spreading | 4.0 | 2. | (D) | 6.5 | * | | 13.0 | 0% | 13.0 |
| 6. ELEMENTAL PHOSPHORUS | | | | | | | | | |
| Ore Handling | 2.0 | 1. | (C) | 6.46 | 25% | (B) | 1.6 | 0% | 1.6 |
| Grinding | 20. | 10. | (C) | 6.46 | 25% | (B) | 16.2 | 97% | .5 |
| Briquetting, Sintering or Nodulizing | 1.3 | 0.65 | (B) | 6.46 | *** | | 4.2 | 60% | 1.7 |
| Furnace Operations | 1.0 | 0.5 | (B) | 6.46 | *** | | 3.2 | 90% | .3 |
| Flares | 1.8 | 0.9 | (B) | 6.46 | *** | | 5.8 | 0% | 5.8 |

TABLE 1 (continued)

| | Uncontrolled Particulate Emission Factor | | Reliability Code | Production Level ($10^6$ tons/yr) | % $P_2O_5$ in Emissions | Reliability Code | $P_2O_5$ Before Controls ($10^3$ tons/yr) | Estimated Level of Emission Control | $P_2O_5$ Emissions After Controls ($10^3$ tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| | (lb/ton) | (Kg/$10^3$ Kg) | | | | | | | |
| 7. PHOSPHORIC ACID (THERMAL) | | | | | | | | | |
| Hydrator-Absorber | 2.6** | 1.3** | (C) | 1.2 | * | - | - | ** | 1.6 |
| 8. SODIUM PHOSPHATE | | | | | | | | | |
| Drying-Cooling & Calcining-Cooling | 60. | 30. | (D) | .8 | * | - | 24. | 90% | 2.4 |
| Material Handling | 2. | 1. | (C) | .8 | * | - | 0.8 | 0% | .8 |
| Grinding | 20. | 10. | (C) | .8 | * | - | 8.0 | 97% | .2 |
| Bagging | 1.0** | 0.5** | (C) | .8 | * | - | - | ** | .4 |
| 9. SOAPS & DETERGENTS | | | | | | | | | |
| Mixing | 40. | 20. | | .6 | * | - | 12. | 98% | .2 |
| 10. CALCIUM PHOSPHATE | | | | | | | | | |
| Drying-Cooling | 60. | 30. | (D) | .2 | * | - | 6.0 | 90% | .6 |
| Material Handling | 2. | 1. | (C) | .2 | * | - | .2 | 0% | .2 |
| Grinding | 20. | 10. | (C) | .2 | * | - | 2.0 | 97% | .1 |
| Bagging | 1.0** | 0.5** | (C) | .2 | * | - | - | ** | .1 |
| Material Handling in Feeding | 2.0 | 1. | (C) | .2 | * | - | .2 | 0% | .2 |

TABLE 1 (continued)

| | Uncontrolled Particulate Emission Factor (lb/ton) | Uncontrolled Particulate Emission Factor ($Kg/10^3 Kg$) | Reliability Code | Production Level ($10^6$ tons/yr) | % $P_2O_5$ in Emissions | Reliability Code | $P_2O_5$ Before Controls ($10^3$ tons/yr) | Estimated Level Emission Control | $P_2O_5$ Emissions After Controls ($10^3$ tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| 11. PLATING, POLISHING, & MISC. | | | | | | | | | |
| Phos. Acid Bath | 0.25** | 0.12 | (D) | .25 | * | | - | ** | .03 |
| 12. INADVERTENT SOURCES | | | | | | | | | |
| a. Refuse Incineration | NA | NA | | 0.15 (uncontrolled Emissions) | 0.23% | (D) | .3 | 37% | .2 |
| b. Iron Mfg. | 150. | 75. | (C) | 245. | 0.2-0.5% ****.35% | (C) | 64. | 90% | 6.4 |
| c. Steel Mfg. | 25. | 12.5 | (C) | 145. | 0.2-0.5% ****.35% | (C) | 6.3 | 90% | .6 |
| d. Cement Mfg. | NA | NA | | 7.8 (uncontrolled Emissions) | .04% | (D) | 3.1 | 88% | 0.4 |
| e. Fuel Oil Combustion | NA | NA | | .287 (uncontrolled Emissions) | .9% | (C) | 2.6 | 0% | 2.6 |
| f. Coal Combustion | NA | NA | | 33.8 (uncontrolled Emissions) | 0.34% | (A) | 115. | 82% | 20.7 |
| | | | | | TOTALS | | 1206.8 | 86.7% | 160.3 |

* Emission Factor multiplier includes % $P_2O_5$

** Emission Factor After Control

*** Emission Factor includes % $P_2O_5$

**** Weighted Average (see text)

NA Not Applicable

D: Below Average

This emission factor is based on engineering estimates made by knowledgeable personnel.

2. Level of Production Activity

This column depicts the quantity of material produced (unless otherwise stated) annually. When multiplied by the emission factor an estimate of the total particulate emissions for that source in lbs. per year is obtained.

The values in this column are based on the material flow calculations presented in Section II. Consequently, they have the same ± 10 percent accuracy as do the material flow values.

3. Percent $P_2O_5$ In Emissions

The method of analyzing or assaying a dust sample for the amount of an element it contains determines to a large extent the reliability of the data. For example, analytical chemistry techniques for dust containing substantial fractions of metal can be accurate to within a small percentage. On the other hand, optical spectroscopy methods for determining concentrations on the order of parts per million can be inaccurate by a factor of 2. Because of this variability, the reliability codes discussed above for the emission factors are also utilized to estimate the relative accuracy of the percentage values listed in Column III.

4. Levels of Phosphorus Emissions Before Control

The values in this column are derived by multiplying the values in columns 1-3. The result is converted to tons/year of emissions before control.

5. Estimated Level of Emission Control

The overall effectiveness of control for a source category is based on two factors:

- the portion of the processes which are under control
- the typical degree of control

For example if 60 percent of vertical roasters have some type of particulate emission control, and these include both scrubbers and precipitators such that the apparent weighted average efficiency of control is 85 percent, the overall control effectiveness is estimated to be 60 x 85 = 51 percent.

The accuracy of control efficiency data varies with the degree of control. For a wet scrubber operating at 80 percent efficiency, i.e. passing 20 percent material, the actual emission may safely be assumed to be between 15 and 25 percent because of the relative ease of making determinations at this level. Thus the emissions after control may be assumed to be accurate within $\pm$ 5/20 or 25 percent. On the other hand, for a baghouse reported as being 99 percent efficient, or passing only 1 percent of the material, the actual emission may vary from 0.5 to perhaps 2 percent because it is frequently difficult to make low-level measurements with accuracy. In such a case, the resulting emission data could be in error by a factor of 2.

Unless otherwise specified, it is assumed that the reported overall level of particulate control applies equally to all phosphorus-containing particles, independent of size, resistance and other important collection parameters. This assumption results in a correct estimate of phosphorus emissions after control when the particulate is chemically homogenious, i.e. phosphorus is contained in the same concentration in all particles. If however, phosphorus is concentrated in certain particles and in addition the efficiency of the control equipment is not uniform for all particles, then the utilization of an average control level is less valid for calculating phosphorus emissions after control. Data on the preferential control of phosphorus-containing particles is seldom available, but is included in this report when possible.

The accuracy of estimating the level of control for a specific source category is dependent on the quality of available data. The investigators feel that, in general, the level of control data will contribute an accuracy to the resulting emissions estimates within $\pm$ 25 percent.

6. Emissions After Control

The values in this column are derived by multiplying the values in Column 4 by the value (100 minus estimated Level of Control).

B. DEVELOPMENT OF EMISSIONS ESTIMATES - 1970

1. Mining Operations

There are three major areas in the U.S. where the phosphate ore is mined: Florida; Tennessee, North Carolina and vicinity; and Western States. The mining techniques which vary with type and grade of rock can be classified into three emissions categories: open pit methods for Florida's land-pebble phosphates; open pit methods for hard rock phosphates; and underground mining.

a. Florida's Land-Pebble Phosphates

Two districts, the central land-pebble and the northern land-pebble produce more than 99 percent of Florida's phosphate rock production. Including North Carolina, 115 million tons of rock were mined.(1) In these places the deposits occur as pebbles ranging from 1/2-inch in diameter to fine sand-sized grains. The ore matrix consists of about 1/3 unconsolidated mixture of phosphate pebbles and fragments of phosphatized limestone, 1/3 silica sand and 1/3 clay.(2,8) The $P_2O_5$ content ranges from 7 to 18 percent. The mining is done by open pit methods using draglines. After stripping about 20 feet of over-burden, the ore is removed, broken up by water jets and stacked at natural ground level in a prepared suction well such that it can be pumped in a slurry form to the washing plant. This wet operation essentially produces no particulate emissions.

b. Open Pit Mining of Hard Rock Phosphates

Hard rock phosphates are found mostly in Tennessee and the Western States. The phosphate rock occurs as coherent plates called lump rock whose grade varies from 18 to 34 percent $P_2O_5$. Draglines mine all of Tennessee's (including Alabama's) production of 5.6 million tons(1) and an estimated 90 percent(9) of the 5.0 million tons

produced in the Western States.[1] The crude ore is either slurried or hauled by trucks or railroad cars to the washer plant where the ore is beneficiated. The mining, loading and hauling will cause small amounts of particulates. A comparison with other mining operations suggests that the particulate emission factor is less than .5 lb per ton of rock used for these operations.[10] Since controls are not applied, total emissions are less than 700 tons $P_2O_5$ per year.

c. Underground Mining

Underground mining, which accounted for about 10 percent of the 5.0 million tons of phosphate rock produced in the Western States, is fading in practice.[9] Mining is restricted mainly to high grade beds ($\geq$ 31 percent $P_2O_5$) which are at the top and base of the phosphatic shale series. The high grade rocks, which vary in size, are used in the production of fertilizers and phosphoric acid, while phosphate shale, which is separated by limestone from the high grade ore and contains about 24 percent $P_2O_5$, is used in the production of elemental phosphorus. The mining method depends on the depth of the ore. Shallow shales are mined by such open-pit methods as top slicing and cut-and-fill, while deep shales are mined underground by room and pillar staging.[8] The ore is transported to plants by railroad cars. The particulate emission of .3 lb. per ton of rock processed was assumed to be less than open pit mining of hard rock because the mining is underground. Total controlled emissions are below 100 tons $P_2O_5$ per year (Table 1).

2. Phosphate Rock Processing

The mined ore is usually beneficiated, crushed and categorized according to a size and grade suitable for subsequent operations or according to purchaser's specifications. The processing operations discussed here are those which prepare the ore for all the other operations discussed in the subsequent sections. Emissions are from washing, grinding, drying, calcining-cooling, material handling at transfer points, conveying systems, and discharge points at storage hoppers, and from open storage.

Beneficiation removes the impurities and improves the grade of the ore by washing, calcining, flotation or combinations of these. The choice depends on the grade and size of the rock. Emissions are negligible from washing and flotation, which is practiced extensively in Florida and moderately in other regions of the southeast and the Western States. Calcining, especially, is practiced in the Western States to burn out the organic material contained in the ore; thus upgrading the phosphate content by 2 to 3 percent (estimated: $4 \times 10^6$ TPY calcined). In some cases where the ore is not calcined, it is dried before grinding (estimate: $35 \times 10^6$ TPY). Only the course rock, >14 mesh, found in Florida is ground, while in the other states more significant grinding is done (estimate: $35 \times 10^6$ TPY ground). These estimates are made in the absence of information as to the quantity of material processed in each of these operations. The estimates refer to quantities of phosphate rock after the removal of two to three times as much waste material. This cleaned rock contains about 30 percent $P_2O_5$.

Several sources of emission factors for these processes are presented in Table 2:

TABLE 2

UNCONTROLLED PARTICULATE EMISSION FACTOR (lb/ton of rock)

| | Midwest Res.[10] | EPA[11] | Source Tests[12] | GCA Estimate |
|---|---|---|---|---|
| Drying | 12 | 15 | 13-62 | 15 |
| Grinding | 2 | 20 | 133 | 20 |
| Calcining | 40 | -- | --- | 40 |
| Material Handling | 2 | 2 | .02-1.32 | 1 |

Emission controls include cyclones and scrubbers. In combination they reduce particulate emissions 95 to 99 percent.[11] Midwest Research published control efficiencies of 94 percent for drying and 97 percent for grinding.[10] They also estimated a 95 percent control efficiency for a cyclone scrubber system for a calcining process. A moderate 50 percent control is estimated for the various processes contributing to material handling losses.

### 3. Wet-Process Phosphoric Acid

Wet-process acid is made commercially in the U.S. by the complete acidulation of ground phosphate rock using sulfuric acid. The reaction is carried out continuously in single or multiple-tank reactors. The considerable amount of heat generated is removed by blowing air over the hot slurry surface or vacuum cooling part of the slurry and recycling it back into the reactor. Then, the calcium sulfate is precipitated and filtered in circular, horizontal tilting-pan vacuum filters. The concentration of the acid is increased from 32 percent $P_2O_5$ to about 54 percent $P_2O_5$ in vacuum evaporators.

Prior to acidulation, the phosphate rock has to be finely ground in a large ball mill. The ground rock is then sent to an air classification system where over-sized particles are recirculated back to the ball mill. The uniform size increases the percent conversion to acid. Although no emission factor data have yet been reported for these ball mills, the emission is assumed similar to the rock grinding discussed earlier. Baghouses or cyclone-scrubber systems assumed to have 97 percent efficiencies are generally employed to control emissions. Approximately 12 million tons of rock are milled in preparation for wet process acid manufacture. With a $P_2O_5$ content of 30 percent, an estimated 36,000 tons per year of uncontrolled $P_2O_5$ emission are generated. After control, an estimated 1,100 tons of $P_2O_5$ emissions are emitted.

Miscellaneous processes of handling the ore before and after grinding also contribute some emission. These processes are estimated to generate 2 lbs/ton of product, twice the rate used above due to the finer grinding employed. Following an estimated 50 percent control, 1,800 TPY of $P_2O_5$ are emitted.

Although the major pollutant from reactors, filters and evaporators is fluoride, phosphoric acid mist is also emitted. Other sources include vents from acid splitter boxes, sumps, and phosphoric acid tanks. These are often vented to scrubbers, which although specifically designed for fluoride emissions, have estimated efficiencies from 98.5 to 100 percent for acid mists.[13] A cooperative study by

Manufacturing Chemists' Association, Inc., and PHS[13] on acid mist emissions reported controlled emission factors from several types of collectors. They ranged from 0 to .50 lb. per ton of $P_2O_5$ produced. The emission factor multiplier is 3,780,000 tons of phosphoric acid expressed as 100 percent $P_2O_5$.

4. Phosphate Fertilizers - General

Phosphates along with the nitrates, urea and sulfates are usually manufactured together in a fertilizer complex and blended to make the basic grades. Although a great deal of information is available on fertilizer production, production processes and plant operation, information on quantities of each fertilizer processed through each unit operation and emissions and control levels are relatively limited and at times contradictory. The major phosphate fertilizer products (DAP, normal superphosphate and triple superphosphate) have common operations which generate significant quantities of $P_2O_5$ as dust. These include materials handling, product screening, bagging, and bulk loading. Fertilizer processes to which rock is added directly, such as normal and triple superphosphate, also have emission from rock pulverization. Control equipment in the various phases include baghouses, electrostatic precipitators, and wet scrubbers.

Emission factors of 6 lb. per ton for rock pulverizing and 2 lb. per ton for material handling were used.[10,11] The same references indicated an average control efficiency of 80 percent for rock pulverizing. The total quantity processed is the sum of the phosphate rock that went into the production of normal and triple superphosphate.[1] Solid fertilizer manufacture generally includes a screening process which provides for product uniformity. Although little information is available on emission factors for screening operations, a general factor of 2 lb. per ton presented by EPA[11] for screening of rock-handling processes is assumed. Controls were assumed to be the same as for the adjacent drying and/or cooling operations.

About 50 percent of the fertilizers are bagged and the operation has a controlled emission factor of 1 lb. per ton.[10] The rest

is shipped in bulk quantity. It is assumed that the emission factor for bulk loading will be less than that for bagging operations.

The following sections describe the manufacturing processes, the particulate emission sources, emission factors and type and efficiencies of control equipment of each of the three major fertilizers.

a. Normal Superphosphate

Normal superphosphate (16 to 22 percent $P_2O_5$) is produced by the den process. Phosphate rock is ground to about 90 percent through 100-mesh screens, and weighed amounts of sulfuric acid and rock are mixed for 1 to 3 minutes in a pan mixer which is fitted with plows which rotate at several rpm. Before the material sets, the soupy mass is discharged into a den below the pan to further react. Batch operations were recently being used by over 75 percent of all U.S. plants.[3]

After the curing period, three alternatives are available.[10] The product can be ground, dried and bagged for sale; sold directly as run-of-pile product; or ammoniated-granulated as a component in mixed fertilizers. Steam or water is used to aid granulation. The mixture is then dried in a rotary drier, cooled, and conveyed to storage bins for bagging or bulk sale.

Emission factors and control efficiencies for grinding, drying and cooling operations were obtained.[10] Because of the varied nature of fertilizer operations, these processes are not always performed on all normal superphosphates produced. However, it is assumed that they are performed on all the 1,366,000 tons of normal superphosphate (as $P_2O_5$) produced.

b. Triple Superphosphate

Commercially, there is little difference between the manufacture of triple and normal superphosphate. Instead of sulfuric acid, phosphoric acid is used for acidulation, and its strength depends on whether the triple superphosphate is to be artificially dried or not. A strength of 70 to 78 percent $H_3PO_4$ may be used if it is dried. After

the last setting step the product is crushed, dried and cooled. Like the normal superphosphate it can be granulated to improve the storage and handling properties of [illegible] directly as run-of-pile or ammoniated and granulated

Emissions [illegible] from [illegible] operations as for the normal superphosphate. Once again it is assumed that all the triple superphosphate produced undergoes the three operations of grinding, drying and cooling.

c. Ammonium Phosphates

Much larger quantities of diammonium phosphates (DAP) are produced than mono-ammonium phosphates. DAP has also been significantly replacing normal and triple superphosphate production.

In producing mono and diammonium phosphates, anhydrous ammonia is passed directly into phosphoric acid to produce either mono or diammonium phosphate. The material is then dried and cooled prior to screening. It is also possible to produce ammonium superphosphates by ammoniating either the normal or triple superphosphate and then using the same drying, cooling and screening steps as discussed above.

Particulate emissions in addition to those included under the general category are primarily from the ammoniator-granulator, dryer and cooler. Emission factors were available for all three. EPA[11] reported factors of 2 lb/ton for an ammoniator-granulator, while NEDS[14] reported 100 and 69 lb/ton for a similar process. An intermediate value of 30 lb/ton is used here. EPA reported 80 lb/ton for a combined dryer-cooler unit. Calculations for an ammonium phosphate cooler, to which GCA had access, showed an uncontrolled emission factor of 25 lb/ton of product and a control level of 80 percent. NEDS indicated from 2.0 to 48 lb/ton for cooling.[14] An intermediate value of 25 lb/ton is used here as being representative of a typical cooling operation. Based on the EPA value for a combined dryer-cooler unit, this leaves 55 lb/ton as an estimated emission factor for drying alone.

The quantity of ammonium phosphates produced are currently unknown due to the unknown totals manufactured from the ammoniation of normal and triple superphosphates. However, the total quantities of ammonium phosphates are estimated to be somewhat less than twice the amount of DAP produced. Using a multiplier of 2, total ammonium and diammonium phosphates produced (as $P_2O_5$) are estimated at 3,500,000 tons. Control efficiencies have been estimated at 80 to 90 percent for the ammoniator-granulator, drying and cooling operations.[9,10] An average 85 percent is used in Table 1.

5. Fertilizer Application

The operation involves receiving the product in bags or bulk quantities and spreading it in the field. Both liquid and granulated fertilizers of different grades are used. Most of the granulated material is in particles from 1 mm to 4 mm in diameter. When the fertilizer is spread, however, many finer particles including those produced by abrasion will enter the atmosphere. The activity of the operation is more intensive than the bulk material handling problems encountered in the fertilizer industry. Emission factors of 1 lb/ton for bulk handling, bagging, loading and 4 lb/ton for spreading are assumed. Control levels of 50 and 0 percent are used. From these assumptions, the handling and spreading of fertilizer expressed as 100 percent $P_2O_5$ is estimated to emit 14,600 tons of $P_2O_5$ into the atmosphere.

Because the quantity of phosphate rock (0.03 million tons) directly applied to the soil is relatively small compared to enriched and mixed fertilizers, the total controlled emissions from bagging-bulk loading and field spreading are negligible.

6. Elemental Phosphorus

An electric arc furnace is employed to manufacture elemental phosphorus. A total of 6,460,000 tons of phosphate rock was processed. The phosphate rock feed, before entering the furnace, must have adequate porosity so that the gases can escape from the reaction zone near the furnace bottom. Briquetting, sintering, and nodulizing

are common methods of attaining the desired porosity. Before these operations, there are emissions from ore handling and grinding operations. The general emission factor of 2 lb/ton was used for ore handling. Although no emission data was available for grinding, a factor of 20 lb/ton is assumed similar to that discussed in phosphate rock processing. The estimated uncontrolled $P_2O_5$ emissions are 16,200 tons for grinding. With a cyclone scrubber system having an efficiency of 97 percent, the controlled emissions are approximately 500 tons.

In the sintering operation, phosphate, sand fines, and coal are blended together and deposited onto moving grates. The mixture then passes over an oil- or gas-fired ignitor where the coal in the bed is set on fire. Both updraft and downdraft sintering machines are utilized, creating sufficient heat to fuse the phosphatic material. The resulting sinter is then crushed and screened with undersized particles recycled. In the nodulizing process, the phosphate fines are heated to incipient fusion in a rotary kiln. The tumbling action in the kiln causes the material to cohere and form spheroidal agglomerates. Briquetting entails mixing phosphate fines and sufficient water to form a damp lump of mass. The briquette is then either dried or calcined to lower the moisture content. These processes are significant generators of $P_2O_5$ emissions. Scrubbers are often employed to reduce fluoride and particulate emissions.

Process information from two large phosphorus plants (million tons per year size) provided emission factors for several sources.[15] In briquetting, a calciner-cooler system was employed with a 65 to 85 percent control efficiency for the calciner and 0 percent control efficiency for the cooler. Based on these data, an emission factor of 1.3 pounds of $P_2O_5$ per ton of rock, before control, was calculated.

The other plant employed nodulizing with a cyclone-scrubber system. A controlled emission factor of 0.27 pound of total particulates per ton of rock was calculated for this plant. Assuming a control efficiency of 90 percent or greater, the emission factor is of the same

order of magnitude as the plant discussed above. For this reason the emission factor of 1.3 lb. $P_2O_5$ per ton of rock processed was selected.

Two general sources of $P_2O_5$ emissions result from furnace operation. There is a problem in preventing $P_2O_5$ fumes from leaking out of the furnace around the electrodes and feed bins. The other source of emissions from the furnace is the tapping operation. Since visible quantities of $P_2O_5$ fumes can result during tapping, many companies are presently installing hoods and ventilation systems to capture the fumes and pass them through high energy scrubbers. A typical phosphorus plant with such a vent system and processing 1.5 million TPY of phosphate rock, had an uncontrolled emission factor of 1.0 lb. of $P_2O_5$/ton of rock and employed a scrubber with a 90 percent control efficiency.[6,15] The furnace operates at 1300 to 1400°C. The hot gases given off by the furnace are comprised of phosphorus and CO gases. After passing through a condenser to recover the phosphorus metal, the exit gas still contains some phosphorus and about 90 percent CO. This gas is often used as a fuel for the sintering operation, while any excess gas, typically 5 percent, is generally vented and flared. Consequently, the flaring emission factors for three plants[9,15] were 0.2, 2.0 and 3.1 lb. of $P_2O_5$/ton of rock. Using an average emission factor of 1.8 lb. $P_2O_5$ per ton of feed, uncontrolled emissions were estimated at 5,800 tons per year. No controls are generally applied to flaring operations.

Other $P_2O_5$ emissions are from the handling of collected dusts from air pollution control devices and from the storage and transfer of phosphorus in the condenser. The collected dust is discharged dry, then usually mixed with water and reprocessed.[16] Since these operations are infrequent and the total quantities are relatively small, the total emissions are estimated to be negligible.

### 7. Thermal Process Phosphoric Acid

This acid is produced from elemental phosphorus in two ways depending upon whether the phosphorus is condensed or not. The "two step" method using the condenser is now more common. The elemental

phosphorus is burned at 1700 to 2800°C using air as the oxygen source. The combustion product is subsequently hydrated and cooled in the hydrator-absorber with dilute phosphoric acid or water. This produces phosphoric acid above 50 percent in strength. Superphosphoric acid usually of strength greater than 70 percent $H_3PO_4$ can be made by limiting the amount of water added.[3,11]

Phosphoric acid mist is a pollutant in the hydrator and absorber tail gas.[10] All plants are equipped with some type of acid mist collection system. Some mist does escape, however, and of this, at least 50 percent of the particles are less than 1.6μ in size. EPA's Compilation of Emission Factors presents the following controlled emission factors:[11]

| | |
|---|---|
| packed tower | 4.6 lb. of mist/ton of acid |
| Venturi scrubber | 5.6 lb. of mist/ton of acid |
| glass-fiber mist eliminator | 3.0 lb. of mist/ton of acid |
| wire mesh mist eliminator | 3.7 lb. of mist/ton of acid |
| high pressure-drop mist eliminator | 0.2 lb. of mist/ton of acid |
| electrostatic precipitator | 1.8 lb. of mist/ton of acid |

Efficiencies for these types of control equipment are well above 90 percent.

Process descriptions by J.C. Barber[16] made it possible to derive and compare the emission factors. Burning phosporus at a rate of 3 tons/hour with a venturi scrubber and single mist eliminator unit having 99.9 percent recovery resulted in controlled emissions of 5-10 lb. of $P_2O_5$/hour. This gives an emission factor of 0.75 - 1.5 lbs. mist per ton of acid. Calculated factors using another data source[17] were .26-4.3 lb. $P_2O_5$/ton $P_2O_5$. Using an average controlled emission factor of 2.6 lbs. $P_2O_5$/ton acid as $P_2O_5$, the annual controlled emissions are estimated at 1,600 tons.

8. Sodium Phosphates

The major marketable compounds are: trisodium phosphate, sodium metaphosphate, tetrasodium pyrophosphate and sodium

tripolyphosphate. The manufacture of these chemicals involves a reaction in a tank, and the separation of the solid, steps which have no emissions. The subsequent operations, calcining or drying, cooling, grinding and bagging, are estimated as typical emission sources of the phosphate industry.[8]

Assuming the emission factors and control efficiencies to be the same as the similar operations previously discussed, the relatively important emissions are from dry-cooling and calcining-cooling operations. An estimated 60 lb/ton and 90 percent control efficiency were assumed for both, based on available information from other processes. Annual production figures for various sodium phosphates,[7] were calculated to have a $P_2O_5$ content of 800,000 tons.

9. Soaps and Detergents

The sodium phosphates are used in soaps, detergents and boiler water treatment as softening agents. By removing calcium and magnesium compounds, scale deposits are avoided in boiler tubes and sticky precipitates are avoided in wash water. Since the operations are wet, it is estimated that emissions are negligible. The soap and detergent manufacturers receive large quantities of sodium phosphates which are used in soaps and detergents. Receiving and handling appears to generate insignificant levels of $P_2O_5$ emissions since the product is received in bags. The mixing operation seems to be the only source. An emission factor of 2 percent and control efficiencies of 98 percent are estimated, based on factors for processes believed to be similar. An estimated 580,000 tons of $P_2O_5$ went into soaps.[3-6]

10. Calcium Phosphates

Calcium phosphate production is estimated to be 200,000 tons per year.[1,3,7] It is produced by two different reactions. The first involves the reaction of $P_2O_5$ gas passing through a column of phosphate rock. This produces molten calcium metaphosphate, which is collected in a pool, tapped, solidified by quenching or air-cooling, ground and bagged. The second involves the reaction of phosphoric acid and lime. The product is dried and then also ground and bagged.

Likely emission sources are drying and cooling, grinding, bagging, and material handling. Emissions from material handling are again generated when calcium phosphates are consumed in animal feeding.

Emission factors for these operations have already appeared in the discussion of other products. The drying or cooling operation with emission factors ranging from 15-105 lbs. per ton (60 lb/ton ave.) generates the only significant emissions. Assuming a 90 percent control efficiency the controlled emissions are 600 tons per year.

### 11. Plating, Polishing and Miscellaneous

There are four important applications in plating and polishing metal surfaces: (1) phosphating or forming a protective layer of insoluble phosphate salt; (2) polishing and brightening the metal surfaces in phosphoric acid baths; (3) electropolishing in phosphoric acid baths; and (4) chemical plating a nickel phosphorus alloy on various surfaces.[5] Approximately 250,000 tons of $P_2O_5$ are consumed for these applications. These operations emit phosphoric acid mist into the atmosphere. Process information to allow formulation of emission factors and types of control is not readily available, but since the emission of mist is similar to the production of phosphoric acid by the wet process, the controlled emission factor is assumed not to exceed 0.25 lb per ton of acid.

Phosphorus is a base of many end products. Many compounds are made such as red phosphorus for matches, phosphorus chloride for organic synthesis, insecticides and plasticizers, phosphorus copper, zinc phosphide, phosphorus sulfide for matches and lubricants, and phosphorus oxides for dehydrating agents. Each transformation is estimated to generate insignificant levels of emissions relative to others already discussed partly because of the small quantities of products made.

## 12. Inadvertent Sources

In addition to the sources from mined phosphates and their subsequent uses, there are other phosphorus emission sources. These include incineration of refuse, the production of large quantities of iron, steel, and cement, and the combustion of residual oils and coal.

### a. Refuse Incineration

Total uncontrolled particulate emissions from refuse incineration (circa 500°C) were estimated in a "Systems Study of Air Pollution from Municipal Incineration"[18] to be 150,000 tons per year. Elsewhere, a slightly higher figure was estimated, using the emission factor of 30 lb per ton[11] with a national figure of 18,000,000 tons[18,19] per year of refuse incinerated. From an analysis of refuse categories, a weighted average phosphorus content was calculated to be 0.23 percent $P_2O_5$ [.05% P x (4.58 lb of $P_2O_5$ per lb of P)]. With an estimated 37 percent efficiency,[18] and an average uncontrolled emission of 250 tons of $P_2O_5$, the total controlled emission was 160 tons of $P_2O_5$.

### b. Iron and Steel Industries

$P_2O_5$ is emitted in trace quantities in the iron and steel industry, where large quantities of particulates are emitted from the various types of furnaces (circa 1500°C). One analysis of the composition of fumes from an open-hearth furnace gave .5 percent $P_2O_5$.[20] A second analysis from an electric-arc furnace contained .2 percent $P_2O_5$.[20] Another analysis from a 15 ton electric-arc steel furnace showed that the dust contained .4 percent $P_2O_5$.[17] An average 0.35 percent $P_2O_5$ content is assumed for all emissions. These sources do not state the methods of analysis, nor the number of samples analyzed which was probably one sample in all cases. Emission factors from a blast furnace are 150 lb/ton and a weighted average for other furnaces in the steel industry is 25 lb/ton.[10] Total production was 245 million tons of iron and 145 million tons of steel.

Controls include a primary cleaner (usually a settling chamber as cyclone) and often a secondary unit connected in series (either a scrubber or electrostatic precipitator). Control efficiencies are estimated at around 90 percent.[11] The controlled emissions are therefore 6400 TPY for iron and 600 TPY for steel manufacturing.

c. Cement

The cement industry also emits large quantities of materials. With a control level of 88 percent, controlled total particulate emissions from the production of cement have been estimated at 934,000 tons/yr.[10] The concentration of $P_2O_5$ in the particulate emissions was not found in the literature and is estimated at .04 percent, equal to the $P_2O_5$ content of average limestone.[21]

d. Oil Burning

Heavy residual oil contains trace quantities of $P_2O_5$. An elemental analysis of total particulates in the flyash from its combustion showed in one test that phosphorus (as $P_2O_5$) amounted to 0.9 percent of total solids collected in a laboratory precipitator at 230°F.[22] Total dust emissions from all types of oil burning are estimated at 287,000 tons/yr.[10] These emissions were almost completely uncontrolled in 1970.

e. Coal

Such large quantities of coal are burned in the U.S. that trace quantities of phosphorus in the emissions make this source significant. Total uncontrolled particulate emissions from the burning of coal is on the order of 33,800,000 tons per year with a weighted control efficiency of 82 percent.[10] Colorimetric analysis of the ash from 373 samples of coal taken from across the U.S. indicated an average phosphorus content of 0.074 percent, equivalent to a $P_2O_5$ content of 0.34 percent.[23] This results in an estimated emission of 20,700 tons of $P_2O_5$ after control. Thus, coal burning is one of the larger sources identified in this study.

Emissions from the mining and cleaning of coal are negligible in comparison to the combustion of coal.

## C. SUMMARY OF PRINCIPAL EMISSIONS

Table 3 summarizes the largest 1970 emissions of phosphorus as the estimates are developed in Table 2. In summarizing, emissions from individual operations are combined within plants of a given type. Also, emissions estimated under the heading "Fertilizer - General" in Table 2 are distributed among the three specific types of fertilizers in proportion to the $P_2O_5$ produced in each of the three classes.

Table 3 groups the emissions in two categories, those directly associated with the phosphorus or phosphorus materials industry; and those having little to do with the phosphorus industry called inadvertent sources. The latter category contributes about 17 percent of total U.S. emissions. The principal sources listed in Table 3 are examined in further detail in later sections of this report.

TABLE 3

PRINCIPAL SOURCES OF PHOSPHORUS-CONTAINING EMISSIONS - 1970

| Phosphorus Industry | U.S. EMISSION (TPY $P_2O_5$) | % OF U.S. |
|---|---|---|
| Triple superphosphate | 35,700 | 22.3 |
| Ammonium phosphate | 30,700 | 19.2 |
| Normal superphosphate | 15,600 | 9.7 |
| Fertilizer application | 14,600 | 9.1 |
| Rock processing | 12,000 | 7.5 |
| Elemental phosphorus | 9,900 | 6.2 |
| Inadvertent Sources | | |
| Coal combustion | 20,700 | 12.9 |
| Iron manufacturing | 6,400 | 4.0 |
| | | 90.9 |

## IV. REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

For purpose of showing geographical distribution, the U.S. was divided into ten regions identical to the Regional Branches of EPA:

| Region | States |
|---|---|
| I | Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont |
| II | New Jersey, New York, Puerto Rico, Virgin Islands |
| III | Delaware, Michigan, Pennsylvania, Virginia, West Virginia, District of Columbia |
| IV | Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee |
| V | Illnois, Indiana, Michigan, Minnesota, Ohio, Wisconsin |
| VI | Arkansas, Louisiana, New Mexico, Oklahoma, Texas |
| VII | Iowa, Kansas, Missouri, Nebraska |
| VIII | Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming |
| IX | Arizona, California, Nevada, Hawaii and the South Pacific |
| X | Alaska, Idaho, Oregon, Washington. |

Emissions from the principal sources listed in Table 3 are listed among these ten regions, as shown in Table 4. Also, the number of plants producing the emissions are shown in the table when such information was available.

The accuracy of the distributions by region varies with the category. The number of plants per category ranged from one to several thousand in this study. When the number of plants was less than 100, an attempt was made to identify each plant and plant location, and include it in one of the ten regions. When production or capacity figures for these plants were available, total production or capacity for each region was computed, and the U.S. emission estimate for that category was distributed by region accordingly. When production or capacity figures were not available, the emission was distributed by the number of plants in each region. If the number of plants was very

## TABLE 4

## REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

| PRINCIPAL SOURCES | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | TOTAL (units) | | REF. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Phosphorus Industry** | | | | | | | | | | | | | |
| Triple Superphos. | 0 | 0 | 0 | 33.1 | 0 | 0 | 0 | .8 | 0 | 1.8 | 35.7 | ($10^3$ TPY) | |
| | 0 | 0 | 0 | 11 | 0 | 0 | 0 | 1 | 0 | 1 | 13 | (Plants) | 24 |
| Ammonium Phos. | 0 | 0 | 0 | 15.5 | .1 | 9.2 | 2.5 | .7 | 1.3 | 1.4 | 30.7 | ($10^3$ TPY) | |
| | 0 | 0 | 0 | 12 | 1 | 8 | 2 | 1 | 7 | 2 | 33 | (Plants) | 24 |
| Normal Superphos. | 0 | 0 | 0 | 13.0 | 0 | 1.8 | 0 | .8 | 0 | 0 | 15.6 | ($10^3$ TPY) | |
| | 0 | 0 | 0 | 15 | 0 | 2 | 0 | 1 | 0 | 0 | 18 | (Plants) | 25 |
| Fertilizer Distrib. | .1 | .3 | .4 | 1.6 | 5.1 | 1.2 | 4.0 | .8 | .5 | .6 | 14.6 | ($10^3$ TPY) | |
| | 0.7 | 1.9 | 3.0 | 11.0 | 34.8 | 8.5 | 27.5 | 5.4 | 3.2 | 4.3 | 100 | (% Bulk Plants) | 26 |
| Rock Processing | 0 | 0 | 0 | 10.5 | 0 | 0 | 0 | .7 | .1 | .7 | 12.0 | ($10^3$ TPY) | |
| | 0 | 0 | 0 | 23 | 0 | 0 | 0 | 7 | 1 | 7 | 38 | (Plants) | 27 |
| Elemental Phosphorus | 0 | 0 | 0 | 5.8 | 0 | .1 | 0 | .4 | 0 | 3.6 | 9.9 | ($10^3$ TPY) | |
| | 0 | 0 | 0 | 9 | 0 | 1 | 0 | 1 | 0 | 3 | 14 | (Plants) | 26 |
| **Inadvertent Sources** | | | | | | | | | | | | | |
| Coal Combustion | .1 | 1.2 | 4.5 | 4.4 | 8.5 | .3 | .8 | .7 | .1 | .1 | 20.7 | ($10^3$ TPY) | |
| | .7 | 5.7 | 21.8 | 21.1 | 41.3 | 1.4 | 4.1 | 3.3 | 0.7 | 0.3 | 100 | (% shipments) | 2 |
| Iron Manufacturing | 0 | .4 | 1.8 | .5 | 3.1 | .3 | 0 | .2 | .1 | 0 | 6.4 | ($10^3$ TPY) | |
| | 0 | 5 | 19 | 7 | 30 | 2 | 0 | 2 | 1 | 0 | 66 | (No. Plants) | 28 |
| TOTALS | 0.2 | 1.9 | 6.7 | 84.0 | 16.8 | 12.9 | 7.3 | 5.1 | 2.1 | 8.2 | 145.6 | ($10^3$ TPY) | |
| | 0.1 | 1.2 | 4.2 | 52.7 | 10.5 | 8.0 | 4.6 | 3.2 | 1.3 | 5.1 | 90.9 | % of U.S. Total | |

small or there was reason to believe that certain plants were larger or produced more emission, distributions were weighted accordingly.

On the other hand, when the estimated number of plants was greater than 100, and the distribution of plants was not known, the regional breakdown was made on a different basis, such as population, geographical area, or shipments reported; whichever seemed to be most appropriate for that category. Whether the distribution was by plant size, number of plants, or another statistic, the distribution is believed to be accurate to within 10 percent in most cases.

Specifically, emissions from the production of triple superphosphate and ammonium phosphate fertilizers were distributed by plant capacity as a percent of total U.S. capacity.[24] In the case of normal superphosphate, since plant capacities were unavailable, distribution was made by number of plants per region.[25]

| | REGION | | | | | | | | | | U.S. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | TOTAL |
| Triple superphosphate | | | | | | | | | | | |
| Capacity* | 0 | 0 | 0 | 1633 | 0 | 0 | 0 | 41 | 0 | 89 | 1763 |
| No. of Plants | 0 | 0 | 0 | 11 | 0 | 0 | 0 | 1 | 0 | 1 | 13 |
| Ammonium Phosphates | | | | | | | | | | | |
| Capacity* | 0 | 0 | 0 | 1423 | 10 | 826 | 225 | 56 | 120 | 127 | 2787 |
| No. of Plants | 0 | 0 | 0 | 12 | 1 | 8 | 2 | 1 | 7 | 2 | 33 |

* (1,000's TPY $P_2O_5$)

Emissions due to the mixing, bagging, and soil application of fertilizers were distributed by the estimated numbers of bulk blend plants in each region, on a percentage basis. A U.S. total of 3,153 plants were estimated in 1966.[26]

Distribution of emissions from rock processing was calculated using the reported capacity of 38 plants engaged in mining activities. It was assumed that processing operations were located near the mines.[27] Distribution of emissions from production of elemental phosphorus was also by reported capacity.

| | REGION | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | TOTAL |
| Rock processing | | | | | | | | | | | |
| Capacity ($10^6$ TPY) | 0 | 0 | 0 | 44.7 | 0 | 0 | 0 | 2.6 | 0.3 | 2.9 | 50.8 |
| No. of Plants | 0 | 0 | 0 | 23 | 0 | 0 | 0 | 7 | 1 | 7 | 38 |
| Elemental Phosphorus | | | | | | | | | | | |
| Capacity ($10^3$ TPY) | 0 | 0 | 0 | 447 | 0 | 10* | 0 | 30 | 0 | 274 | 761 |
| No. of Plants | 0 | 0 | 0 | 9 | 0 | 1 | 0 | 1 | 0 | 3 | 14 |

*estimate

The two sources classed as "inadvertent" were distributed as follows. Emissions from the combustion of coal were distributed by tonnage of coal shipped, by state of destination,[1] on a percentage basis. Emissions from the production of iron were distributed by the amount of iron and steel scrap and pig iron consumed in each state, making estimates where data had been withheld.[1] The number of plants operating blast furnaces in 1970 was reported to be 66:[28]

| | REGION | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | TOTAL |
| Metal consumed ($10^6$ TPY) | 0 | 5.5 | 25.4 | 7.0 | 44.4 | 4.5 | 0 | 3.4 | 1.7 | 0 | 92.2 |
| No. of Plants | 0 | 5 | 19 | 7 | 30 | 2 | 0 | 2 | 1 | 0 | 66 |

As a result of these assumptions, the principal emission sources are distributed most heavily in Region 4, where an estimated 84,400 TPY of $P_2O_5$ is released into the atmosphere. This is about 53 percent of the U.S. total emission, and is the result of concentrated phosphate operations of several kinds, especially in the states of Florida and Tennessee. Region 4 is also the region with the greatest emission per unit geographical area, having an estimated 0.22 tons of $P_2O_5$ per square mile-year.

## V. NATURE OF EMISSIONS

Emissions of particulate containing phosphorus depend both on the conditions of the emitting process, and on the characteristics of the element phosphorus and its compounds. From the chemist's viewpoint, phosphorus is located in the periodic table between nitrogen and arsenic and is not considered a metal. Phosphorus is similar to nitrogen in some respects, forming numerous compounds ranging from the simple to the complex. These range from the phosphates essential in metabolism, to other compounds which are extremely toxic such as phosphine ($PH_3$) and halogenated compounds including phosphorus pentabromide ($PBr_5$), pentachloride ($PCl_5$) and pentafluoride ($PF_5$).

Table 5 lists some of the principal physical properties of phosphorus.

TABLE 5

PHYSICAL PROPERTIES OF PHOSPHORUS*

| | |
|---|---|
| Melting point: | 44°C |
| Boiling (vaporization) point: | 280°C (B. Pt. of $P_2O_3$ = 174°C) |
| Density: | 1.82 g/cm$^3$ |
| Atomic weight: | 31.0 a.w.u. |
| Heat of vaporization: | 3.0 kg-cal/g atom |
| Valence (oxidation states): | +5, -3, and +3 commonly, and all states from +5 to -3 occasionally |

The properties that are most pertinent to this study includes the ability of phosphorus to form many kinds of compounds, due to its numerous possible oxidation states; the tendency of its oxides (phosphorus oxide, $P_2O_3$ or $P_4O_6$; and phosphoric oxide or pentoxide, $P_2O_5$ or $P_4O_{10}$) to react rather quickly with water vapor to form phosphoric acid, $H_3PO_4$; and the vaporization temperature which is low when compared to many of the processes used in the industry.

*Ref. 29, Table 3-160

## A. FERTILIZER EMISSIONS

Particles emitted from fertilizer processes range from finely divided rock to finished fertilizer. Rock particles tend to be large and thus tend to settle near the emission point, although a small quantity of submicrometer dust from drilling and crushing may be expected to travel distances on the order of miles before deposition. Rock particles contain tricalcium phosphate, in concentrations ranging from 15 to 80 percent equivalent weight of $P_2O_5$. This phosphate is stable and insoluble until reacted.

The fertilizer product superphosphate, both normal and triple, is monocalcium phosphate which is stable and partially soluble. Particles of normal superphosphate also contain gypsum. They occasionally contain dicalcium phosphate which is also partially soluble. Triple superphosphate is non-hygroscopic. Ammonium and diammonium phosphates are stable, white powders and are soluble in water.

Particle sizes in fertilizer emissions are not well described in the literature. It was reported that 12 percent (by weight) of the emission from a superphosphate dryer consisted of particles of less than 10 micrometers in diameter.[10] These particles were described as hot, moist, partially water soluble, corrosive, odorous, and able to adhere to almost any surface. Other fume particles of ammonium chloride, and fluoride-containing particles are also emitted.

## B. ELEMENTARY PHOSPHORUS EMISSIONS

Electric furnace emissions include, in addition to phosphorus vapor, possible variable quantities of lime, silica, alumina, and magnesia particulate. The furnace temperature is 1300 to 1400°C, at which temperature the vapor is believed to be in the form $P_4$. When it cools to 800°C and below, at least part of the vapor becomes $P_2$.

Most of the vapor is trapped under water by hot water sprays, in which it condenses to the liquid "metal". Vapor that escapes and reacts quickly with oxygen to form $P_2O_5$ which changes quickly to acid, $H_3PO_4$ in the presence of moisture. $P_2O_5$ is extremely

hygroscopic. The other oxide, $P_2O_3$ which forms in limited oxygen concentrations, also quickly becomes phosphoric acid. Therefore it appears from basic chemistry that most of the phosphorus emission is in very fine droplets of phosphoric acid. These are probably hygroscopic, and grow slowly as they travel, until gravitation or other natural processes remove them from the atmosphere.

Condensed phosphorus is described as a yellow, wax-like solid (below 44°C) which ignites spontaneously in air, forming oxides. This is the reason for keeping it under water. Steam vapors from the surface of the water, although possessing a repelling odor, may include extremely low concentrations of dilute phosphoric acid.

"White" phosphorus is $P_4$ vapor; and "red" phosphorus is thought to be the same molecule joined in chains. In the proper atmosphere these are fairly stable, but otherwise they are reactive and poisonous. Although the emissions from the production of phosphorus contain these materials, they probably very quickly become acid on exposure to air.

C. PHOSPHORIC ACID PLANT EMISSIONS

Particulate emissions from a thermal acid plant have been described:[30]

2 percent less than 0.5 micrometer in diameter
30 percent less than 1 micrometer in diameter
85 percent less than 2 micrometers in diameter
99 percent less than 3 micrometers in diameter

Particle densities are 1.57 to 1.68 $g/cm^3$, indicating high acid content, and are described as corrosive and irritating.[10]

Combustion of phosphorus in thermal acid manufacture is at 1700 to 2800°C. Presumably all of the phosphorus is sufficiently oxidized and then hydrated to acid, so that no toxic emissions result.

D. OTHER SOURCES

Under certain conditions, heating phosphorus to high temperatures in the presence of halogens can result in the formation of

toxic compounds such as phosphorus chloride.[31] This in turn reacts with water to form $PH_3$ (phosphine gas) which is highly toxic.* Phosphine has been used in the fumigation of wheat, with some toxic effects to workers.[32] The emission of these toxic compounds from the production of phosphoric acid has not been reported, but is cited here as an apparent possibility.

A large number of phosphorus compounds are made specifically for their toxic or poisonous properties, for fumigation, insecticides, etc. While the small quantity of these compounds has precluded them from this report, their contribution to the emission of toxic phosphorus compounds may be significant.

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* A dye called phosphine contains no phosphorus; also, note that the poisonous gas phosgene contains no phosphorus.

## VI. UPDATING OF EMISSIONS ESTIMATES

The following recommendations are made for periodically updating the estimates made in this study:

### A. VERIFICATION OF CURRENT ESTIMATES

1. Although phosphate fertilizer manufacture is the largest source of $P_2O_5$ emissions, very little data exists for accurately determining emissions levels and degree of control from this source category. The emissions and control values presented for this source category warrant further verification, although the general conclusion regarding the magnitude of the emissions from this source category, we feel, is valid.

2. Verify the high levels of control indicated for phosphate rock processing as the category generates a significant quantity of emissions before control.

3. $P_2O_5$ emissions from normal superphosphate manufacture were distributed within geographic regions by the number of plants since plant capacities were unavailable. Such capacities should be obtained and the geographic distribution verified.

### B. PERIODIC REVIEW OF ESTIMATES

1. The Bureau of Mines estimates for material flow, industry practices, and trends, provide the best estimates of the size of the industry.

2. EPA activities are currently generating the best emissions data and should be reviewed using:

   a. Overall industry studies, e.g. references (6)(27).
   b. The Source Test Program in which specific individual plant emissions are measured. This information provides emission factors for specific examples of typical industrial operations, and also provides some analyses of the particulate, usually including trace metal content and particle size.

c. NEDS (National Emissions Data System) is steadily being enlarged and improved. This system can provide emission factors for specific plants and plant operations, the type of particulate control equipment in use, and the actual, or estimated, control efficiency. The system may eventually be expanded to include a description of the emissions.

3. The phosphorus industry should be consulted for its opinion and suggestions on the most recently published estimates. This may be best accomplished by interviewing the Phosphorus Commodity Specialist, Division of Non-ferrous Metals, Bureau of Mines in Washington; or by interviewing one or more of the principal companies in the industry.

4. The literature should be reviewed, using (a) industrial views as published from time to time in Chemical Engineering, for example, and (b) environmental views as summarized in Pollution Abstracts, for example.

5. Individual companies or plants may be approached for opinions, data, or cooperative tests of their own operations. It is difficult to obtain fresh information in this way, due to the natural reluctance of plants to discuss environmental problems. However, data thus obtained have a relatively high degree of reliability.

6. State agencies in which specific plants are located may be able to provide useful information, and should be contacted.

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